

DECLARATION

I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/230,704 filed on September 7, 2000.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 20th day of October, 2000


Atsuko Ikeda

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Method for Purification of Tetrafluoromethane and Use
Thereof

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for purification of tetrafluoromethane, comprising contacting tetrafluoromethane containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities with zeolite having an average pore size of 3.4 to 11 Å and/or a carbonaceous adsorbent having an average pore size of 3.4 to 11 Å to reduce said impurities.

[Claim 2] The method for purification of tetrafluoromethane as claimed in claim 1, wherein tetrafluoromethane containing said impurities is contacted with zeolite and/or a carbonaceous adsorbent in the liquid phase.

[Claim 3] The method for purification of tetrafluoromethane as claimed in claim 1 or 2, wherein the Si/Al ratio of said zeolite is 1.5 or less.

[Claim 4] The method for purification of tetrafluoromethane as claimed in any one of claims 1 to 3, wherein said zeolite is at least one selected from the group consisting of MS-4A, MS-5A, MS-10X and MS-13X.

[Claim 5] The method for purification of tetrafluoromethane as claimed in claim 1 or 2, wherein said carbonaceous adsorbent is Molecular Sieving Carbon 4A and/or Molecular Sieving Carbon 5A.

[Claim 6] The method for purification of tetrafluoromethane as claimed in any one of claims 1 to 5, wherein said ethylene compounds are at least one compound selected from the group consisting of ethylene, fluoroethylene, difluoroethylene and tetrafluoroethylene.

[Claim 7] The method for purification of tetrafluoromethane as claimed in claim 6, wherein said ethylene compounds are ethylene and/or tetrafluoroethylene.

[Claim 8] The method for purification of tetrafluoromethane as claimed in any one of claims 1 to 5, wherein said hydrocarbon compounds are at least one compound selected from the group consisting of methane, ethane and propane.

[Claim 9] The method for purification of tetrafluoromethane as claimed in claim 8, wherein said hydrocarbon compounds are methane and/or ethane.

[Claim 10] The method for purification of tetrafluoromethane as claimed in any one of claims 1 to 9, wherein the total content of ethylene compounds, hydrocarbon compounds, carbon monoxide and carbon dioxide

contained in tetrafluoromethane is reduced to 3 ppm or less.

[Claim 11] The method for purification of tetrafluoromethane as claimed in any one of claims 1 to 10, wherein tetrafluoromethane containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities is produced by a direct fluorination method of reacting trifluoromethane with fluorine gas.

[Claim 12] The method for purification of tetrafluoromethane as claimed in any one of claims 1 to 10, wherein tetrafluoromethane containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities is produced by a direct fluorination method of reacting carbon with fluorine gas.

[Claim 13] A tetrafluoromethane product having a purity of 99.9997 mass% or more, which is obtained by performing the purification according to the method described in any one of claims 1 to 12.

[Claim 14] An etching gas comprising the tetrafluoromethane product described in claim 13.

[Claim 15] A cleaning gas comprising the tetrafluoromethane product described in claim 13.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates a method for purification of tetrafluoromethane (hereinafter referred to as "FC-14" or " CF_4 ") and use thereof.

[0002]

[Background Art]

FC-14 is used as an etching gas or a cleaning gas, for example, in the manufacturing process of semiconductor devices, therefore, a high-purity product thereof is demanded.

With respect to the production method for FC-14, various methods have heretofore been proposed. To speak specifically, for example, the following methods are known:

(1) a method of reacting dichlorodifluoromethane with hydrogen fluoride in the presence of a catalyst;

(2) a method of reacting monochlorotrifluoromethane with hydrogen fluoride in the presence of a catalyst;

(3) a method of reacting trifluoromethane with fluorine gas;

(4) a method of reacting carbon with fluorine gas;
and

(5) a method of thermally decomposing tetrafluoro-

ethylene.

[0003]

However, these methods for producing FC-14 have a problem in that intermediates of FC-14 or by-products produced by the reaction or impurities derived from raw materials form an azeotropic mixture or an azeotrope-like mixture with the objective FC-14 and the separation thereof is extremely difficult. To cope with this, for example, a purification method of treating FC-14 containing trifluoromethane (CHF_3) as impurities with zeolite or a carbonaceous adsorbent has been proposed (see, Japanese Patent No. 2,924,660).

[0004]

[Problems to be Solved by the Invention]

Heretofore, however, an industrially advantageous method is not known, where FC-14 containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities is purified and thereby high-purity FC-14 almost free of these impurities can be obtained with good profitability.

The present invention has been made under these circumstances and the object of the present invention is to provide a purification method where FC-14 is contacted with an adsorbent to remove by adsorption those impurities and

thereby high-purity FC-14 can be obtained in an industrially advantageous manner with good profitability.

[0005]

[Means to Solve the Problems]

As a result of extensive investigations to solve the above-described problems, the present inventors have found that in the process of producing high-purity FC-14, when FC-14 containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities is contacted with an adsorbent comprising zeolite having specific average pore size and Si/Al ratio and/or a carbonaceous adsorbent (Molecular Sieving Carbon) having a specific average pore size, the impurities can be selectively adsorbed and removed and high-purity FC-14 almost free of impurities can be obtained. The present invention has been accomplished based on this finding. The present invention provides a method for purification of tetrafluoromethane and use thereof, described in (1) to (15) below.

[0006]

(1) A method for purification of tetrafluoromethane, comprising contacting tetrafluoromethane containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities with zeolite having an

average pore size of 3.4 to 11 Å and/or a carbonaceous adsorbent having an average pore size of 3.4 to 11 Å to reduce the impurities.

(2) The method for purification of tetrafluoromethane as described in (1) above, wherein tetrafluoromethane containing the impurities is contacted with zeolite and/or a carbonaceous adsorbent in the liquid phase.

(3) The method for purification of tetrafluoromethane as described in (1) or (2) above, wherein the Si/Al ratio of the zeolite is 1.5 or less.

(4) The method for purification of tetrafluoromethane as described in any one of (1) to (3) above, wherein the zeolite is at least one selected from the group consisting of MS-4A, MS-5A, MS-10X and MS-13X.

(5) The method for purification of tetrafluoromethane as described in (1) or (2) above, wherein said carbonaceous adsorbent is Molecular Sieving Carbon 4A and/or Molecular Sieving Carbon 5A.

[0007]

(6) The method for purification of tetrafluoromethane as described in any one of (1) to (5) above, wherein the ethylene compounds are at least one compound selected from the group consisting of ethylene, fluoroethylene, difluoroethylene and tetrafluoroethylene.

(7) The method for purification of tetrafluoromethane as described in (6) above, wherein the ethylene compounds are ethylene and/or tetrafluoroethylene.

(8) The method for purification of tetrafluoromethane as described in any one of (1) to (5) above, wherein the hydrocarbon compounds are at least one compound selected from the group consisting of methane, ethane and propane.

(9) The method for purification of tetrafluoromethane as described in (8) above, wherein the hydrocarbon compounds are methane and/or ethane.

(10) The method for purification of tetrafluoromethane as described in any one of (1) to (9) above, wherein the total content of ethylene compounds, hydrocarbon compounds, carbon monoxide and carbon dioxide contained in tetrafluoromethane is reduced to 3 ppm or less.

[0008]

(11) The method for purification of tetrafluoromethane as described in any one of (1) to (10) above, wherein tetrafluoromethane containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities is produced by a direct fluorination method of reacting trifluoromethane with fluorine gas.

(12) The method for purification of tetrafluoromethane as described in any one of (1) to (10) above, wherein

tetrafluoromethane containing ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities is produced by a direct fluorination method of reacting carbon with fluorine gas.

(13) A tetrafluoromethane product having a purity of 99.9997 mass% or more, which is obtained by performing the purification according to the method as described in any one of (1) to (12) above.

(14) An etching gas containing the tetrafluoromethane product described in (13) above.

(15) A cleaning gas containing the tetrafluoromethane product described in (13) above.

[0009]

In summary, the present invention provides "a method for purification of tetrafluoromethane, comprising contacting FC-14 containing ethylene compounds, hydrocarbons, carbon monoxide and/or carbon dioxide as impurities with zeolite and/or a carbonaceous adsorbent each having an average pore size of 3.4 to 11 Å to reduce the impurities", "a tetrafluoromethane product having a purity of 99.9997 mass% or more, which is obtained by performing the purification according to the above-described method", and "an etching gas and a cleaning gas containing the above-described tetrafluoromethane product".

[0010]

[Mode for Carrying Out the Invention]

For producing FC-14, for example, a method of reacting trifluoromethane with fluorine gas, a method of reacting carbon with fluorine gas and a method of thermally decomposing tetrafluoroethylene are known. When these methods are used, FC-14 obtained contains ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities due to impurities in the raw materials, for example, organic trace impurities, trace oxygen, trace water content or the like.

[0011]

The ethylene compounds contained is at least one compound selected from ethylene ($\text{CH}_2=\text{CH}_2$), monofluoroethylene ($\text{CH}_2=\text{CHF}$), difluoroethylene ($\text{CH}_2=\text{CF}_2$) and tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$).

The hydrocarbon compounds contained is at least one compound selected from methane (CH_4), ethane (C_2H_6) and propane (C_3H_8).

[0012]

The boiling points of the objective FC-14 and those impurities under atmospheric pressure are shown in Table 1 below.

[Table 1]

Compound Name	Chemical Formula	Boiling Point (°C)
Carbon monoxide	CO	-191.5
Methane	CH ₄	-161.5
FC-14	CF ₄	-128
Ethylene	CH ₂ =CH ₂	-103.7
Ethane	CH ₃ CH ₃	-89
Difluoroethylene	CH ₂ =CF ₂	-83
Carbon dioxide	CO ₂	-78.5
Tetrafluoroethylene	CF ₂ =CF ₂	-76.3
Monofluoroethylene	CH ₂ =CHF	-72
Propane	CH ₃ CH ₂ CH ₃	-42.1

[0013]

These impurities are very difficult to separate by a distillation operation because the objective FC-14 forms an azeotrope-like mixture therewith or as seen from Table 1, the boiling points are approximated. To cope with this, in an ordinary distillation operation, the number of stages of the distillation tower is increased or the number of distillation towers is increased to reduce the impurities as much as possible, however, this is not profitable and moreover, high-purity FC-14 almost free of these impurities can be hardly obtained.

[0014]

In the present invention, for selectively adsorbing and removing those impurities in FC-14, zeolite having an average pore size of 3.4 to 11 Å and/or a carbonaceous adsorbent (Molecular Sieving Carbon) having an average pore size of 3.4 to 11 Å is used as the adsorbent. For measuring the average pore size, a gas adsorption process using Ar gas may be used.

The adsorbent is more preferably (1) zeolite having an average pore size of 3.4 to 11 Å and an Si/Al ratio of 1.5 or less, (2) a carbonaceous adsorbent having an average pore size of 3.4 to 11 Å (Molecular Sieving Carbon) or (3) an adsorbent obtained by adding a carbonaceous adsorbent having an average pore size of 3.4 to 11 Å to zeolite having an average pore size of 3.4 Å to 11 Å and an Si/Al ratio of 1.5 or less. The Si/Al ratio as used herein is an atomic ratio.

[0015]

Specific examples of the impurities in FC-14, which can be removed by using these adsorbents, include unsaturated compounds such as ethylene, monofluoroethylene, difluoroethylene and tetrafluoroethylene, hydrocarbon compounds such as methane, ethane and propane, and oxygen-containing compounds such as carbon monoxide and carbon

dioxide. As the impurities, preferred are ethylene, tetrafluoroethylene, methane, ethane, carbon monoxide and carbon dioxide, and more preferred are ethylene and ethane.

[0016]

The difference in the molecular size between the objective FC-14 and those impurities is small, therefore, selective adsorption and removal of the impurities in FC-14 can be hardly attained only by the difference in the molecular size. In the present invention, by taking account of polarity and pore size of the adsorbent, the following three kinds of adsorbents are used as an adsorbent which can selectively adsorb and remove the impurities.

[0017]

The first adsorbent is zeolite having an average pore size of 3.4 to 11 Å, preferably zeolite having an Si/Al ratio of 1.5 or less. Specific examples thereof include MS-4A. MS-4A has an average pore size of about 3.5 Å and an Si/Al ratio of 1.0. By performing an adsorption operation using this zeolite, the contents of ethylene, tetrafluoroethylene, methane, ethane, carbon monoxide and carbon dioxide as impurities can be reduced. Depending on the kind of zeolite, the impurity content can be reduced even to 5 ppm or less and thereby, high-purity FC-14 can be obtained.

[0018]

Even when the Si/Al ratio is 1.5 or less, if the average pore size is less than 3.4 Å, for example, in the case of zeolite having a pore size of about 3.2 Å, reduction in the impurity content cannot be verified.

Even when the Si/Al ratio is 1.5 or less, in the case of zeolite having an average pore size in excess of 11 Å, reduction in the impurity content cannot be verified.

Furthermore, even when the average pore size is from 3.4 to 11 Å, in the case of zeolite having an Si/Al ratio in excess of 1.5, reduction in the impurity content cannot be verified.

[0019]

The second adsorbent is a carbonaceous adsorbent (Molecular Sieving Carbon) having an average pore size of 3.4 to 11 Å. For example, a carbonaceous adsorbent having an average pore size of about 4 Å, like the above-described zeolite, can reduce the impurity content to 5 ppm or less and thereby, high-purity FC-14 can be obtained.

However, in the case of a carbonaceous adsorbent having an average pore size in excess of 11 Å, reduction in the impurity content cannot be verified and, for example, in the case of activated carbon having an average pore size of about 35 Å, which is commonly used and exhibits strong

adsorption activity, almost no reduction of impurities is verified.

[0020]

The third adsorbent is an adsorbent obtained by adding (mixing) a carbonaceous adsorbent (second adsorbent) having an average pore size of 3.4 to 11 Å to zeolite (first adsorbent) having an average pore size of 3.4 to 11 Å and an Si/Al ratio of 1.5 or less. Depending on the kind of this adsorbent, the impurity content can be reduced even to 3 ppm or less and thereby FC-14 having higher purity can be obtained. This is considered to occur because zeolite has an excellent function of adsorbing particularly carbon monoxide, carbon dioxide and the like, whereas the carbonaceous adsorbent has an excellent function of adsorbing particularly unsaturated compounds and the like, and when these two adsorbents are used in combination, an effect attributable to the combination use is brought out.

[0021]

The above-described zeolite and carbonaceous adsorbent can be used as a sole adsorbent but two or more kinds of the adsorbents may also be used in combination at an arbitrary ratio. In the case of the third adsorbent, the mixing ratio between zeolite and the carbonaceous adsorbent can be changed according to the concentration of impurities.

[0022]

The ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide as impurities contained in FC-14 are not particularly limited on the concentration, however, the concentration is preferably 0.1 mass% or less, more preferably 0.05 mass% or less.

In the case where impurities other than those described above, for example, perfluorocompounds such as FC-116 (CF_3CF_3) and FC-218 (C_3F_8) are intermixed in the objective FC-14, the perfluorocompounds can be separated and removed by performing a distillation operation either before or after the step of treatment with the above-described adsorbent.

[0023]

In the method for purification of FC-14 according to the present invention, the method of contacting FC-14 containing impurities with an adsorbent is not limited and for example, FC-14 containing impurities may be contacted in the gaseous phase, by the gas-liquid contacting or in the liquid phase. Among these, the method of contacting FC-14 containing impurities in the liquid phase is efficient and preferred.

For contacting FC-14 containing impurities in the liquid phase, a known method such as batch system or

continuous system may be used, however, in industry, a method of providing, for example, two units of fix bed-type absorption towers and when one unit reaches its saturated adsorption, the unit is changed over and subjected to regeneration is generally employed.

[0024]

At the time of contacting FC-14 containing impurities with an adsorbent, the treating temperature, the treated amount and the treating pressure are not particularly limited, however, the treating temperature is preferably low and suitably from -50°C to 50°C . The treating pressure may suffice if, in the case of liquid phase, the liquid phase can be maintained and in the case of gaseous phase, the treating pressure is not particularly limited.

[0025]

As described in the foregoing pages, by using the method for purification of the present invention, ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide contained in FC-14 can be effectively adsorbed and removed and thereby high-purity FC-14 can be obtained. The purity of FC-14 obtained is 99.9997 mass% or more and for the analysis of FC-14 products having a purity of 99.9997 mass% or more, (1) gas chromatography (GC) using TCD method, FID method (each including the precut method)

or ECD method, or (2) an analysis instrument such as gas chromatography mass spectrometer (GC-MS) may be used.

[0026]

The high-purity FC-14 can be used as an etching gas at the etching step in the process of producing a semiconductor device. Furthermore, the high-purity FC-14 can be used as a cleaning gas at the cleaning step in the process of producing a semiconductor device. In the production process of a semiconductor device such as LSI and TFT, a thin or thick film is formed using a CVD method, a sputtering method or a vapor deposition method and the film is etched to form a circuit pattern. In the apparatus for forming the thin or thick film, cleaning is performed to remove unnecessary deposits accumulated on the inner wall of the apparatus, jig and the like, because unnecessary deposits cause generation of particles and must be removed on occasion for producing a good-quality film.

[0027]

In the etching using FC-14, the etching may be performed under various dry etching conditions such as plasma etching and microwave etching, and FC-14 may be used by mixing it with an inert gas such as He, N₂ and Ar, or with a gas such as HCl, O₂ and H₂, at an appropriate ratio.

[0028]

[Examples]

The present invention is described in greater detail below by referring to the Examples and Comparative Examples, however, the present invention should not be construed as being limited to these Examples.

[Raw Material Example 1 of FC-14]

Carbon was reacted with fluorine gas in the presence of a diluting gas, unreacted fluorine gas was removed, and the product gas rich in FC-14 was purified by fractional distillation according to a conventional method. Then, the product gas was analyzed by gas chromatography, as a result, the obtained FC-14 had the composition shown in Table 2 below.

[0029]

[Table 2]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF_4	99.9688
Carbon monoxide	CO	0.0006
Carbon dioxide	CO_2	0.0056
Methane	CH_4	0.0012
Ethylene	$\text{CH}_2=\text{CH}_2$	0.0112
Tetrafluoroethylene	$\text{CF}_2=\text{CF}_2$	0.0028
Ethane	CH_3CH_3	0.0098

[0030]

[Raw Material Example 2 of FC-14]

Difluoromethane (CH_2F_2) was reacted with fluorine gas in the presence of a diluting gas, then the reacted gas was introduced into an alkali cleaning tower to remove hydrogen fluoride generated and a slight amount of unreacted fluorine gas. The product gas rich in FC-14 was purified by fractional distillation according to a known method and analyzed by gas chromatography, as a result, the obtained FC-14 had the composition shown in Table 3 below.

[0031]

[Table 3]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF_4	99.9722
Carbon monoxide	CO	0.0005
Carbon dioxide	CO_2	0.0025
Methane	CH_4	0.0004
Monofluoroethylene	$\text{CH}_2=\text{CHF}$	0.0056
Difluoroethylene	$\text{CH}_2=\text{CF}_2$	0.0038
Tetrafluoroethylene	$\text{CF}_2=\text{CF}_2$	0.0108
Trifluoromethane	CHF_3	0.0042

[0032]

(Example 1)

Into a 200 ml-volume stainless steel-made cylinder,

20 g of zeolite [Molecular Sieves 4A (produced by Union Showa K.K., average pore size: 3.5 Å, Si/Al ratio: 1)] was filled and vacuum dried, then about 70 g of FC-14 of Raw Material Example 1 was filled while cooling the cylinder, and the contents were occasionally stirred while keeping the temperature at -20°C. After about 8 hours, the liquid phase part was analyzed by gas chromatography. The analysis results are shown in Table 4 below.

[0033]

[Table 4]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF ₄	99.9992
Carbon monoxide	CO	<0.0001
Carbon dioxide	CO ₂	<0.0001
Methane	CH ₄	<0.0001
Ethylene	CH ₂ =CH ₂	<0.0001
Tetrafluoroethylene	CF ₂ =CF ₂	0.0003
Ethane	CH ₃ CH ₃	0.0001

[0034]

As is apparent from the results in Table 4, by using zeolite having an average pore size of 3.5 Å and an Si/Al ratio of 1 as the adsorbent, impurities in FC-14 can be reduced and the impurity content can be reduced to 10 ppm or less.

[0035]

(Example 2)

Into a 200 ml-volume stainless steel-made cylinder, 20 g of zeolite [Molecular Sieves 13X (produced by Union Showa K.K., average pore size: 10 Å, Si/Al ratio: 1.23)] was filled and vacuum dried, then about 70 g of FC-14 of Raw Material Example 1 was filled while cooling the cylinder, and the contents were occasionally stirred at room temperature (about 18°C). After about 8 hours, the liquid phase part was analyzed by gas chromatography. The analysis results are shown in Table 5 below.

[0036]

[Table 5]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF ₄	99.9991
Carbon monoxide	CO	<0.0001
Carbon dioxide	CO ₂	<0.0001
Methane	CH ₄	<0.0001
Ethylene	CH ₂ =CH ₂	0.0003
Tetrafluoroethylene	CF ₂ =CF ₂	0.0002
Ethane	CH ₃ CH ₃	0.0001

[0037]

As is apparent from the results in Table 5, by using zeolite having an average pore size of 10 Å and an Si/Al

ratio of 1.23 as the adsorbent, impurities in FC-14 can be reduced and the impurity content can be reduced to 10 ppm or less.

[0038]

(Example 3)

Into a 200 ml-volume stainless steel-made cylinder, 20 g of carbonaceous adsorbent [Molecular Sieving Carbon, produced by Takeda Yakuhin Kogyo K.K., average pore size: 4 Å] was filled and vacuum dried, then about 70 g of FC-14 of Raw Material Example 2 was filled while cooling the cylinder, and the contents were occasionally stirred at room temperature (about 18°C). After about 8 hours, the liquid phase part was analyzed by gas chromatography. The analysis results are shown in Table 6 below.

[0039]

[Table 6]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF ₄	99.9992
Carbon monoxide	CO	0.0001
Carbon dioxide	CO ₂	0.0002
Methane	CH ₄	0.0001
Monofluoroethylene	CH ₂ =CHF	<0.0001
Difluoroethylene	CH ₂ =CF ₂	<0.0001
Tetrafluoroethylene	CF ₂ =CF ₂	<0.0001
Trifluoromethane	CHF ₃	0.0001

As is apparent from the results in Table 6, by using a carbonaceous adsorbent having an average pore size of 4 Å [Molecular Sieving Carbon] as an adsorbent, impurities in FC-14 can be reduced and the impurity content can be reduced to 10 ppm or less.

[0040]

(Example 4)

Into a 200 ml-volume stainless steel-made cylinder, 15 g of zeolite [Molecular Sieves 4A (produced by Union Showa K.K., average pore size: 3.5 Å, Si/Al ratio: 1)] mixed with 15 g of a carbonaceous adsorbent [Molecular Sieving Carbon, produced by Takeda Yakuhin Kogyo K.K.: average pore size of 4 Å] was filled and vacuum dried, then

about 70 g of FC-14 of Raw Material Example 1 was filled while cooling the cylinder, and the contents were occasionally stirred at room temperature (about 18°C). After about 8 hours, the liquid phase part was analyzed by gas chromatography. The analysis results are shown in Table 7 below.

[0041]

[Table 7]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF ₄	99.9994
Carbon monoxide	CO	<0.0001
Carbon dioxide	CO ₂	<0.0001
Methane	CH ₄	<0.0001
Ethylene	CH ₂ =CH ₂	<0.0001
Tetrafluoroethylene	CF ₂ =CF ₂	<0.0001
Ethane	CH ₃ CH ₃	<0.0001

[0042]

To determine the content of trace impurities, microanalysis was performed by gas chromatography using TCD method, FID method (including precut method) or ECD method, or by an analysis instrument such as gas chromatography mass spectrometer (GC/MS), and from the values obtained, the purity was calculated. The results are shown in Table 8.

[0043]

[Table 8]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF ₄	99.9998
Carbon monoxide	CO	<0.4 ppm
Carbon dioxide	CO ₂	<0.4 ppm
Methane	CH ₄	<0.3 ppm
Ethylene	CH ₂ =CH ₂	<0.1 ppm
Tetrafluoroethylene	CF ₂ =CF ₂	<0.2 ppm
Ethane	CH ₃ CH ₃	<0.2 ppm

As is apparent from the results in Table 8, the purity of FC-14 obtained is 99.9997 mass% or more.

[0044]

(Comparative Example 1)

Into a 200 ml-volume stainless steel-made cylinder, 20 g of zeolite [Molecular Sieves XH-9 (produced by Union Showa K.K., average pore size: 3.2 Å, Si/Al ratio: 1)] was filled and vacuum dried, then about 70 g of FC-14 of Raw Material Example 1 was filled while cooling the cylinder, and the contents were occasionally stirred at room temperature (about 18°C). After about 8 hours, the liquid phase part was analyzed by gas chromatography. The analysis results are shown in Table 9 below.

[0045]

[Table 9]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF ₄	99.9698
Carbon monoxide	CO	0.0004
Carbon dioxide	CO ₂	0.0051
Methane	CH ₄	0.0012
Ethylene	CH ₂ =CH ₂	0.0111
Tetrafluoroethylene	CF ₂ =CF ₂	0.0027
Ethane	CH ₃ CH ₃	0.0097

As is apparent from the results in Table 9, even when the Si/Al ratio is 1, if the average pore size of zeolite is less than 3.4 Å, almost no reduction of impurities can be verified.

[0046]

(Comparative Example 2)

Into a 200 ml-volume stainless steel-made cylinder, 20 g of zeolite [H-ZSM-5 (produced by N.E. Chemcat K.K., average pore size: 6 Å, Si/Al ratio: 75)] was filled and vacuum dried, then about 70 g of FC-14 of Raw Material Example 1 was filled while cooling the cylinder, and the contents were occasionally stirred at room temperature (about 18°C). After about 8 hours, the liquid phase part was analyzed by gas chromatography. The analysis results

are shown in Table 10 below.

[0047]

[Table 10]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF_4	99.9733
Carbon monoxide	CO	0.0003
Carbon dioxide	CO_2	0.0047
Methane	CH_4	0.0009
Ethylene	$\text{CH}_2=\text{CH}_2$	0.0098
Tetrafluoroethylene	$\text{CF}_2=\text{CF}_2$	0.0021
Ethane	CH_3CH_3	0.0089

As is apparent from the results in Table 10, even when the average pore size is 6 Å, if the Si/Al ratio of zeolite exceeds 1.5, almost no reduction of impurities can be verified.

[0048]

(Comparative Example 3)

Into a 200 ml-volume stainless steel-made cylinder, 20 g of a carbonaceous adsorbent [activated carbon, Particulate SHIROSAGI KL, produced by Takeda Yakuhin Kogyo K.K., average pore size: 35 Å] was filled and vacuum dried, then about 70 g of FC-14 of Raw Material Example 2 was filled while cooling the cylinder, and the contents were occasionally stirred at room temperature (about 18°C).

After about 8 hours, the liquid phase part was analyzed by gas chromatography. The analysis results are shown in Table 11 below.

[0049]

[Table 11]

Compound Name	Chemical Formula	Purity (mass%)
FC-14	CF ₄	99.9795
Carbon monoxide	CO	0.0004
Carbon dioxide	CO ₂	0.0021
Methane	CH ₄	0.0003
Monofluoroethylene	CH ₂ =CHF	0.0038
Difluoroethylene	CH ₂ =CF ₂	0.0026
Tetrafluoroethylene	CF ₂ =CF ₂	0.0079
Trifluoromethane	CHF ₃	0.0034

As is apparent from the results in Table 11, with a carbonaceous adsorbent having an average pore size in excess of 11 Å, reduction of impurities cannot be verified.

[0050]

[Effects of the Invention]

According to the present invention, tetrafluoromethane containing impurities which had been heretofore very difficult to remove, particularly ethylene compounds, hydrocarbon compounds, carbon monoxide and/or carbon dioxide, is contacted with zeolite having an average pore